Inquiries at the Interface

Scientists find small effects play huge role in how materials evolve

You might call them "control freaks" of sorts. Ultimately, they'd like nothing better than the ability to guide what happens every step of the way, and they're making remarkable progress in that direction.

Don't misunderstand — Ames Laboratory researchers Rohit Trivedi, Ralph Napolitano and James Morris are great guys, but relentless in their desire to better understand how microstructures develop in materials. Working toward that objective, they're studying certain properties that exist in metals at the interface between the liquid and solid phases during solidification.

"We want to have control of the microstructure," says Napolitano, physical metallurgist and an Iowa State University assistant professor. To gain that control, he says, "We need to understand the fundamental principles that underlie microstructural evolution, beyond simply tweaking the process knobs." The three scientists are focusing their basic research efforts on that goal – one that may some day allow them and others to tailor microstructural development, providing the basis for new and improved materials.

What lies between

The Ames Laboratory team has shown that there are many subtle variations in microscopic properties at the liquid-solid interface as the solid is "freezing out." The small variations depend upon which crystal face is in contact with the liquid. Different faces, or orientations, give slightly different values for properties such as free energy, mobility, and stiffness (surface tension); and these properties play dramatic roles in how the microstructure of a metal evolves during solidification.

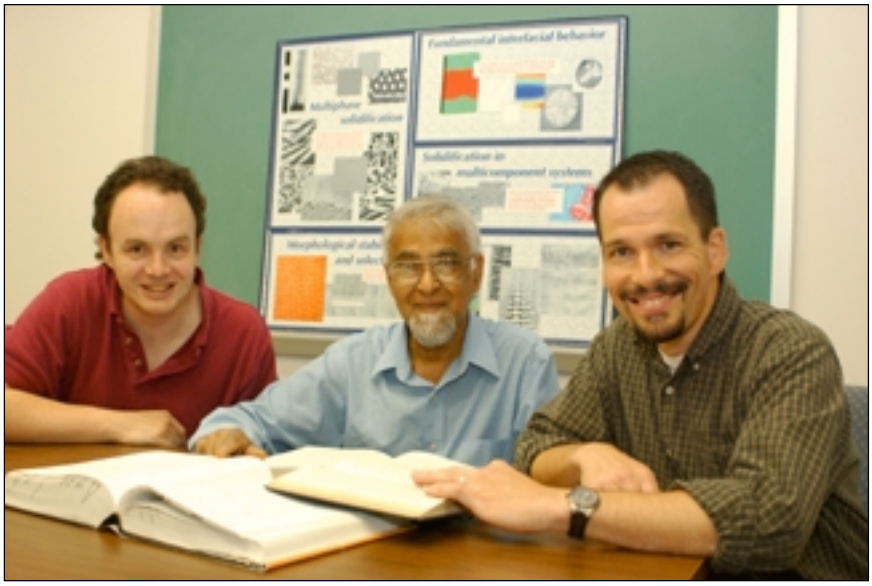
"If one examines the interface between a solid and a liquid, it is found that the structure observed is strongly dependent upon the crystallographic plane with which the liquid is in contact," says Napolitano. "In metals, this dependence is particularly interesting because the interface is typically 'atomistically rough' and is continuously fluctuating, so that the crystallography can only be represented statistically. It is the nature of these variations at the atomistic level that ultimately governs the overall behavior of the interface," he explains. Accordingly, Napolitano notes that a complementary relationship between his and Trivedi's experimental approach and the theoretical predictions of Morris, a theoretical physicist, has developed quite naturally. "At the end of the day, the fundamental knowledge we're gaining about crystallographic dependence of interfacial properties is critical to the development of various theories concerning solidification, crystal growth, and the natural evolution of microstructure in materials," he says.

Trivedi, physical metallurgist and an ISU distinguished professor, provides some insight into the importance of the interfacial properties he and his co-workers are investigating. "There are some properties that are extremely small, but they have a profound influence on interfacial behavior," he says. "For example, the way a snowflake forms depends on very small factors. It turns out that some of these small factors are really the essential ones in determining shape. The same thing is true not only for materials, but for humans, animals, plants – anything that grows. People generally ignore this, but we're finding out that they simply cannot."

A couple of "firsts"

Trivedi, Napolitano and Morris are paying close attention to the small factors and their effects on microstructural evolution. "We're investigating some very specific quantities, such as the variation of interfacial free energy with crystallographic orientation," says Napolitano. He and Trivedi have developed innovative experimental techniques that provide the first reliable measurements of the minuscule variations in free energy at the liquid-solid interface in metallic systems. Morris' complementary calculations represent the first (and so far only) effort to theoretically predict the variation in interfacial free energy for aluminum. The combined efforts of the three scientists provide both a direct check between the experiment and the simulation and the opportunity to put forth new solidification theories. Napolitano continues, "By revealing the essential physical behavior of liquid-solid interfaces, these critical experiments, both experimental and theoretical, are facilitating significant advancement in the theoretical prediction of microstructures."

Morris produces molecular dynamics simulations of coexisting liquid and solid phases, such as the one shown here, to see how the atoms behave at the interface. In this image, the darker region in the center represents the disordered atoms of the liquid phase. The lighter regions on either side represent the ordered atoms of the solid phase.



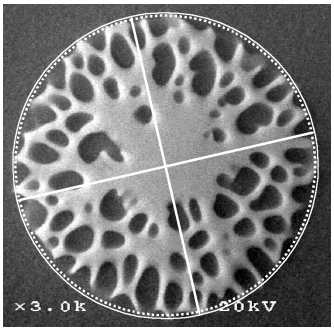
(left to right) Researchers James Morris, Rohit Trivedi and Ralph Napolitano are studying the fundamental interfacial behavior between liquid and solid phases during the solidification of metals with the ultimate goal being the ability to control microstructural development.

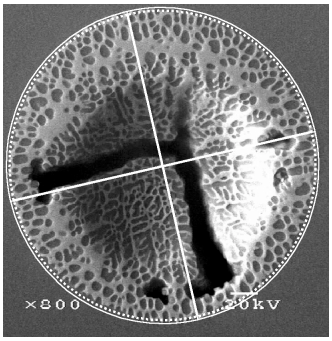
The metallurgists' method

In experiments designed to measure small effects on the property of interfacial free energy, Trivedi and Napolitano have devised a method to selectively melt certain microscopic regions within an aluminum alloy single crystal, forming a dispersion of tiny liquid droplets trapped within the solid. (A single crystal is one in which the atoms are arranged according to a single "plan" or "template." The orientation is uniform throughout the material, creating a simple, symmetric structure.) The material is then heated to bring the droplet structures to equilibrium (the condition at which no change occurs in the state of a system unless its surroundings are altered). After rapid quenching, the droplet shapes are measured very carefully, and their equilibrium shapes are determined, providing the necessary link to interfacial properties. "Thermodynamics tells us how the equilibrium droplet shape is related to the interfacial free energy," says Napolitano. "These measurements provide a direct means for quantifying the subtle variation of this property with respect to crystallographic orientation. The challenge is to accurately measure the degree to which the droplet shapes deviate from being spherical, and they deviate only by a percent or so."

Napolitano (left) and Trivedi place an aluminum alloy single-crystal into a furnace to selectively melt certain microscopic regions, forming and trapping a dispersion of tiny liquid droplets within the solid. While this melting proceeds rapidly, stabilization of the droplet dispersion may require several weeks. Morris (seated) watches the laboratory procedure with interest. A theorist, his lab is his computer.

Trivedi adds, "When you look at the droplets with your eyes, they look like spheres. It's only when you magnify and measure them precisely that you find the spheres are altered in certain directions, so there's a different energy in different directions."





The two-phase structures that form within the droplets during rapid quenching from the liquid state reveal the overall pre-quench equilibrium shapes of the droplets. Trivedi and Napolitano use such cross sections to quantify the deviation from sphericality in the quenched droplets. The deviation is extremely small, but enough to effect big changes in microstructural development.

The physicist's process

Getting a clearer picture of just how little the equilibrium droplet shape deviates from a true sphere is Morris' job. "You're looking at this droplet and saying, 'Well, this droplet isn't perfectly spherical; it has some small asymmetry.' We want to measure that, and we don't want it influenced by dirt in the system or anything else," says Morris. "The deviation is a very small number, but it's very important, and that's where doing the calculations and modeling the atomic fluctuations of the liquid-solid interface have come in."

Based on the results of Trivedi's and Napolitano's experiments, Morris selects a model for how the atoms interact to calculate the variations in interfacial properties. To do so, he uses molecular dynamics simulations of the liquid-solid interfaces at equilibrium. His work shows how the atoms behave at the interface and allows him to track their equilibrium fluctuations to calculate interfacial free energy. "You're completely relying on whether the potentials used can provide accurate calculations, and in this case there's been no previous comparison of an experimental measurement with a detailed atomistic calculation," says Morris. "This is a first, and the fact that the comparisons come out nicely suggests that these potentials are suitable."

Small but mighty

Trivedi emphasizes again that the small effects dominate throughout nature. "It's very obvious in biology — think of gene expression in the development of the human embryo. Many things can go wrong, but by and large they don't," he says. "The same thing is true for the development of microstructures in metals. There are very fundamental issues that govern what happens. We would like to know precisely how they influence microstructure formation. To do that, we need to understand the small effects. We study metals, but the principles we hope to generate will have much broader applications." ■

~ Saren Johnston

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